

# Electronic properties and hyperfine fields of nickel-related complexes in diamond

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## Abstract

We carried out a first principles investigation on the microscopic properties of nickel-related defect centers in diamond. Several configurations, involving substitutional and interstitial nickel impurities, have been considered either in isolated configurations or forming complexes with other defects, such as vacancies and boron and nitrogen dopants. The results, in terms of spin, symmetry, and hyperfine fields, were compared with the available experimental data on electrically active centers in synthetic diamond. Several microscopic models, previously proposed to explain those data, have been confirmed by this investigation, while some models could be discarded. We also provided new insights on the microscopic structure of several of those centers.

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## I. INTRODUCTION

Diamond is a material which stands alone in nature, carrying a unique combination of electronic, mechanical, thermal, and optical properties. Diamond is the hardest known natural material, having a large bulk modulus, high thermal conductivity and a large electronic band gap. Those properties make it a prototypical material to a number of applications, ranging from drilling and cutting tools to electronic devices to operate under extreme conditions<sup>1</sup>. More recently, new potential applications for doped diamond have been proposed, such as superconducting materials<sup>2</sup> and quantum computing<sup>3,4</sup>.

There are two major methods with widespread use to grow macroscopic samples of synthetic diamond. Chemical vapor deposition (CVD) methods produce high quality diamond thin films grown over large areas. On the other hand, the high pressure-high temperature (HPHT) processes produce bulk diamond at relatively high growth rates and low costs. In those processes, samples are grown out of graphite, using 3d transition metal (TM) alloys (involving nickel, cobalt, and iron) as solvent-catalysts. Nickel is the only impurity that has been unambiguously identified in the resulting diamond. Such residual nickel impurities, either isolated or forming complexes with other defects, can generate several electrically and optically active centers<sup>5</sup>. Understanding the nature and microscopic structure of those centers is crucial in developing diamond-related technologies. Following the experimental identification of those centers, several microscopic models have been proposed to explain such data. However, there is still considerable controversy over a unified model which could explain most of those active centers in diamond. Here, we used first principles calculations to address this question.

Over the last decade, nickel-related impurities in diamond have been investigated by several theoretical approaches<sup>6-9</sup>. However, no investigation has provided a comprehensive picture of most of the nickel-related active centers identified in diamond so far. We used first principles total energy calculations, based on the full-potential linearized augmented plane wave methodology<sup>10</sup>, to investigate the structural and electronic properties of those centers in terms of the spin, symmetry, ground state multiplet, formation and transition energies, and hyperfine parameters. We focused our investigation on centers involving isolated nickel, either in interstitial or substitutional configurations, and complexes involving nickel and vacancies or dopants (boron and nitrogen). This paper is organized as follow:

in section II we discuss the available electron paramagnetic resonance (EPR) experimental data of nickel-related defects in diamond. In section III, we present the methodology used in this investigation. Sections IV and V present and discuss the results in the context of experimental data.

## II. A SURVEY ON THE EXPERIMENTAL DATA

Electron paramagnetic resonance and optical absorption measurements have been used to identify a number of nickel-related active centers in diamond, and have been recently reviewed<sup>5</sup>. The electronic properties of those centers have been analyzed in terms of either the Ludwig-Woodbury (LW)<sup>11</sup> or the vacancy<sup>12</sup> model. According to the LW model, when a  $3d^n4s^2$  ion ( $1 \leq n < 9$ ) occupies an interstitial site in a type-IV semiconductor, its 4s electrons are transferred to the 3d orbitals, resulting in a  $3d^{n+2}$  configuration. In the tetrahedral crystal field, the 3d states are split into  $e + t_2$  irreducible representations. The threefold  $t_2$  states lie lower in energy than the two-fold  $e$  states. This level ordering is the result of the octahedral crystal field, created by the next nearest neighbors of the impurity, which is stronger than the tetrahedral crystal field from the nearest neighbors. The same ion in a substitutional site would present a  $3d^{n-2}$  configuration, since four electrons are needed to bind with the four nearest neighboring host atoms. However, in this case the crystal field has tetrahedral symmetry, driving the  $e$  states to lie lower in energy than the  $t_2$  ones. Additionally, in the LW model, the gap levels are filled according to the Hund's rule. The LW model is schematically presented in fig. 1.

For substitutional impurities, there is an alternative model, called the vacancy model, proposed by Watkins for TM elements near the end of the 3d, 4d, and 5d series<sup>12</sup>. This model proposed that the electronic structure of the impurity resulted from a weak interaction between the impurity-related  $d-t_2$  states and the  $t_2$  vacancy-related ones, as represented in fig. 1. The vacancy-related states came from the dangling bonds on the host atoms surrounding the vacant site into which the transition metal was inserted. As a result, the impurity band gap states would have a vacancy-like behavior. Although those two models were developed to describe the properties of 3d-transition metal impurities in silicon, they have been extensively used to explain the microscopic properties of those impurities in other semiconductors, such as nickel-related impurity centers in diamond.

Nickel in diamond has been detected in a tetrahedral symmetry with a spin  $S=3/2$  by EPR<sup>13</sup> and optical measurements<sup>14</sup>, and has been labeled W8 center. The microscopic model suggested for this center, based on either the LW or vacancy models, is an isolated substitutional nickel in the negative charge state ( $\text{Ni}_\text{s}^-$ ) in a  $3d^7$  configuration<sup>13</sup>.

Two major active centers have been found in synthetic diamond, which have been associated to interstitial nickel, labeled NIRIM-1 and NIRIM-2 centers<sup>15</sup>. The NIRIM-1 has been identified with a spin  $S=1/2$  in a trigonal symmetry at low temperatures ( $T < 25$  K), which switches to a tetrahedral symmetry at higher temperatures. This center was discussed in the context of the LW model, and interpreted as resulting from an isolated interstitial nickel in the positive charge state ( $\text{Ni}_\text{i}^+$ )<sup>15</sup>. Since substitutional nickel in a positive charge state would give a spin  $S=5/2$  according to the LW model, it was ruled out as a possible microscopic configuration for the NIRIM-1 center. More recently, independent investigations suggested that this center could, in fact, be formed by  $\text{Ni}_\text{s}^+$ , giving a spin  $S=1/2$ <sup>8,16</sup>, indicating that the vacancy model is more suitable to describe this center.

The NIRIM-2 center has been identified with a spin  $S=1/2$  with a strong trigonal distortion<sup>15,17,18</sup>. The microscopic structure of this center is still the subject of controversy. It was initially associated to an interstitial nickel with an impurity or vacancy nearby<sup>15</sup>. More recently, this center has been proposed to be formed by a complex of nickel and boron<sup>16</sup> or even by an isolated interstitial  $\text{Ni}^8$ .

Post-growth annealing treatments introduce new active centers in the as-grown samples, which have been labeled NE centers<sup>19</sup>. It has been suggested that those NE centers involve nickel, nitrogen and vacancies. The NE4 center, that displays a  $D_{3d}$  symmetry and a spin  $S=1/2$ , has been tentatively associated to an interstitial Ni sitting in the middle position of a divacancy. This vacancy-nickel-vacancy unit ( $\text{VNiV}$ ) would be aligned along a  $\langle 111 \rangle$  direction. This configuration has also been labeled as  $\text{NiC}_6$  in the literature, which represents, besides the impurity, the six nearest neighboring carbon atoms. The LW model<sup>11</sup> was invoked to describe this configuration, in which the Ni impurity would donate six of its ten d-electrons to form bonds to the six neighboring carbon atoms. The remaining four 3d electrons should occupy a triplet d-orbital, according to Hund's rule. Since the center has a spin  $S=1/2$ , then this center should be in the negative charge state  $(\text{VNiV})^-$ , associated to a  $t_2^5$  electronic configuration. The NE4 center is the precursor to several other NE centers, which are formed by replacing nearest neighboring carbon atoms with nitrogen ones<sup>19</sup>, in

a  $\text{NiC}_{6-m}\text{N}_m$  ( $1 \leq m \leq 6$ ) configuration. Recently, a center with rhombohedral symmetry and spin  $S=1$ , has been observed in diamond<sup>20</sup>. A (VNiV) configuration was suggested for this center, similar to that of NE4, but here in the neutral charge state. The NE1 center has a monoclinic symmetry and spin  $S=1/2$ , and has been suggested to be formed by a (VNiV) configuration plus two nearest neighboring nitrogen atoms<sup>21</sup>. The NE8 center has a monoclinic symmetry and spin  $S=1/2$ , and has been suggested to be formed by a (VNiV) configuration plus four nearest neighboring nitrogen atoms<sup>21</sup>.

EPR data has unambiguously shown that nickel can pair with boron and nitrogen impurities in diamond, forming new active centers. A center, labeled NOL1, has been identified with spin  $S=1$  and trigonal symmetry<sup>21</sup>. It has been suggested that this center is formed by an interstitial  $\text{Ni}_i^{2+}(3d^8)$  impurity axially distorted by a boron ( $\text{B}_s^-$ ) along a  $\langle 111 \rangle$  direction, with an unspecified interatomic distance between the impurities. A more recent examination of the trigonal boron-related NOL1 center suggested a different model, that would involve substitutional nickel and boron,  $\text{Ni}_s^+\text{B}_s^0$ , with the acceptor boron in a next nearest neighboring site, with no covalent bonding between the impurities<sup>16</sup>.

In samples with high concentrations of both nickel and nitrogen, other active centers have been identified. In addition to the NE centers, the AB5 center, with a spin  $S=1$  and trigonal symmetry, has been identified<sup>22</sup>. The microscopic model proposed for this center is a substitutional nickel ( $\text{Ni}_s^{2-}$ ) with a nearby substitutional nitrogen atom ( $\text{N}_s^+$ ). Table I summarizes the properties of nickel-related EPR active centers in diamond, as well as the respective proposed microscopic models.

Most of the microscopic models proposed in the previous paragraphs have been built based on an ionic model<sup>24</sup>, which has been proposed to describe the 3d-transition metal-acceptor pairs  $\text{TM}_i^+-\text{A}_s^-$  in silicon<sup>11</sup> (TM in a tetrahedral interstitial site in a positive charge state plus an acceptor A in a negative charge state). According to that model, the pair stable configuration corresponds to a classical system consisting of a  $\text{TM}_i^+$  electrostatically bound to a nearest neighbor  $\text{A}_s^-$  embedded in a dielectric medium<sup>25</sup>. Since the negatively charged acceptor has a closed shell, the electronic properties of the pair can be directly related to the positive TM ion placed in a screened Coulomb field.

### III. METHODOLOGY

We used the all-electron spin-polarized full-potential linearized augmented plane wave (FP-LAPW) method<sup>10</sup>, implemented in the WIEN2k package<sup>26</sup>. The calculations were performed within the framework of the density functional theory, using the Perdew-Burke-Ernzerhof exchange-correlation potential<sup>27</sup>. All the calculations were performed considering a 54-atom reference supercell. The methodology separates the crystalline space in two distinct regions: the atomic and interstitial ones. The electronic wave functions were expanded in terms of spherical harmonics in the atomic regions and of plane waves in the interstitial ones. We chose all atomic spheres with a radius of  $R = 0.64 \text{ \AA}$ . Therefore,  $2R$  was much smaller than the crystalline interatomic distance of  $1.54 \text{ \AA}$ , such that atomic sphere overlap was avoided even in the case of large atomic relaxations. We used a  $2 \times 2 \times 2$  grid to sample the irreducible Brillouin zone as well as the  $\Gamma$ -point.

Convergence in the total energy was tested by varying the number of plane waves describing the electronic wave-functions in the interstitial region, a  $7.0/R$  value provided converged results. Self-consistent interactions were performed until total energy and the total charge in the atomic spheres changed by less than  $10^{-4} \text{ eV/atom}$  and  $10^{-5}$  electronic charges/atom between two iterations, respectively. Additionally, the atomic positions were relaxed until the forces were smaller than  $0.02 \text{ eV/\AA}$ . All those approximations and convergence criteria have been shown to provide an accurate description of several defect centers in semiconductors<sup>28-30</sup>.

Formation and transition energies of all centers were computed using the procedure discussed in Ref.<sup>28</sup>. The procedure required the total energies of the respective defect center and the chemical potentials of carbon, nitrogen and nickel. Those chemical potentials were computed using the total energy of carbon in a diamond lattice, nitrogen in a  $\text{N}_2$  molecule, and nickel in a FCC lattice. In order to compute the hyperfine tensors, spin-orbit coupling was included in a second-variational procedure. Additional information concerning the calculation of hyperfine tensors is presented in Appendix.

## IV. RESULTS

We considered most of the proposed microscopic models for the electrically active centers described in table I, as well as, other possible models for those centers. Figure 2 represents the diamond lattice in the  $(1\bar{1}0)$  plane, showing the possible sites in which the impurities could be placed in the beginning of each simulation. All atomic positions were later relaxed, according to convergence criteria discussed in the previous section.

### A. Isolated Nickel

Substitutional nickel in diamond was considered in several charge states, with the results summarized in table II. In the case of the neutral charge state ( $\text{Ni}_s^0$ ), the center has no point-symmetry ( $C_1$ ), and presents a spin  $S=1$ . This configuration is only 0.1 eV more stable than the center in a  $C_{3v}$  symmetry ( $\text{Ni}_s^{0*}$ ). Figure 3 displays the induced energy eigenvalues in the gap region for substitutional nickel impurity. The gap states of  $\text{Ni}_s$  are vacancy-like orbitals, consistent with the vacancy model<sup>12</sup>.

Table II also presents the results for interstitial nickel. In the positively charge state ( $\text{Ni}_i^+$ ), the center was initially simulated in a trigonal ( $C_{3v}$ ) symmetry, in order to check if that configuration could explain the properties of the NIRIM-2 center<sup>8</sup>. In that symmetry, it presented an effective spin  $S=1/2$  and an  $^2E$  multiplet ground state. By releasing the symmetry constraint, there was an energy gain of about 0.2 eV, and the center distorted to a  $C_{1h}$  symmetry. This symmetry lowering was very small, corresponding to a distortion on the nickel atom of only 0.06 Å toward one of its second nearest neighbors, breaking the trigonal symmetry. Figure 4 compares the electronic structure of the  $\text{Ni}_i^+$  center in both symmetries, showing that although the symmetry lowering was small, there were strong effects in the electronic structure of the center. These results show that the electronic structure of interstitial nickel cannot be described by the LW model<sup>11</sup>, since the 3d-nickel related states remain resonant in the valence band, leaving a hole in the perturbed valence band top. In trigonal symmetry, the valence band top of the diamond crystal splits into an  $a_1$  state, resonant in the valence band, and an  $e$  state, occupied by three electrons, inside the gap. In the  $C_{1h}$  symmetry, the  $e$  gap states split further in an  $a'$  and an  $a''$  ones.

## B. Ni-vacancy complexes

We initially considered an interstitial nickel paired with a nearest neighboring vacancy ( $\text{Ni}_i\text{V}$ ), as suggested as a stable configuration in several experiments<sup>15</sup>. However, this configuration was unstable and the impurity moved toward the vacant site, forming a substitutional nickel<sup>8</sup>. We additionally considered a substitutional nickel paired with a nearest neighboring vacancy ( $\text{Ni}_s\text{V}$ ), but in the final relaxed structure, the nickel remained in the middle position between two vacancies ( $\text{VNiV}$ ). Figure 5 presents the induced energy eigenvalues of this last complex and table II presents the respective properties.

The electronic structure of the  $\text{VNiV}$  complex cannot be described by the LW model, as it has been recently suggested<sup>19</sup>. Our results indicate that the relevant electronic properties of this center should be associated to divacancy-like orbitals, which appeared in the gap, while the Ni-related orbitals remained resonant and inert inside the valence band. On the other hand, the electronic structure is well described by the crystal field theory, in which the electronic states can be interpreted as resulting from an interaction between the divacancy states and those of the Ni atom. The one-electron ground state structure of a diamond divacancy in  $D_{3d}$  symmetry has the  $a_{2u}^2 a_{1g}^2 e_u^2 e_g^0$  configuration. In that symmetry, the Ni 3d energy levels are split into  $2e_g + a_{1g}$ . When a Ni atom is placed in the middle position of a divacancy, its  $e_g$  energy level interacts with the carbon dangling bonds, leaving a fully occupied non-bonding  $t_{2g}$ -like ( $e_g + a_{1g}$ ) orbital inside the valence band. On the other hand, the Ni  $e_g$  state interacts with the divacancy  $e_g$  gap level, leaving the  $e_g$ -bonding level in the valence band and the  $e_g$ -anti-bonding one unoccupied in the gap. The relevant electronic properties of this center are related to the  $e_u$  divacancy-like orbital, which remained in the gap bottom. In the positive and negative charge states, the symmetry lowering ( $D_{3d} \rightarrow C_{2h}$ ) is very weak and the splitting in the  $e_u$ -related states is smaller than 0.1 eV.

## C. Ni-B complexes

We now consider complexes involving nickel and substitutional boron, which could potentially lead to a trigonal symmetry, to be consistent with proposed models for Ni-B centers presented in table I. For interstitial nickel-substitutional boron pairs, we considered three microscopic configurations, according to figure 2:  $\text{Ni}_i\text{B}_s$  pair, with Ni and B respectively



in sites 6 and 1;  $\text{Ni}_i\text{CB}_s$  pair, with Ni and B respectively in sites 6 and 4; and  $\text{Ni}_i\otimes\text{B}_s$  with Ni and B respectively in sites 7 and 1. Table III presents the properties of those centers in several charge states. The  $(\text{Ni}_i\text{B}_s)^{0*}$  complex, has a degenerate configuration in  $\text{C}_{3v}$  symmetry, coming from the partially occupied  $e$  state, favoring a symmetry lowering to  $\text{C}_1$ . The distance between the Ni and B in the pairs is crucial for the final properties of those centers, as evidenced by the electronic structure of those three centers, in the same charge state, shown in figure 6. The major difference emerges on the character of the highest occupied level in the center. While for the  $\text{Ni}_i\text{B}_s$  and  $\text{Ni}_i\text{CB}_s$  pairs, this level has a localized Ni 3d-related character, for the  $\text{Ni}_i\otimes\text{B}_s$ , this level is essentially delocalized. For this last center, the distance between the impurities is so large that the center can be well described by an ionic model, in which the role of boron is only to accept an electron from the nickel impurity. Therefore, the electronic structure of this complex can be well described as an isolated interstitial nickel in 2+ charge state ( $\text{Ni}^{2+}$ ).

For substitutional nickel-substitutional boron, we considered two structural configurations, according to figure 2:  $\text{Ni}_s\text{B}_s$  pair, with Ni and B respectively in sites 3 and 4;  $\text{Ni}_s\otimes\text{B}_s$  pair, with Ni and B respectively in sites 1 and 5. Figure 7 presents the energy eigenvalues of those pairs and table III summarizes their properties. In the  $\text{Ni}_s\otimes\text{B}_s$  centers, boron is far from the nickel impurity, working as just an acceptor, such that the electronic configuration resembles that of isolated substitutional Ni impurity, shown in figure 3. For the  $\text{Ni}_s\text{B}_s$  pair, boron plays a more important role, affecting the electronic structure of the center, although the magnetic properties of this center are associated with partially occupied energy levels with prevailing nickel character.

#### D. Ni-N complexes

The nickel and nitrogen complexes in diamond are generally formed as result of high-temperature thermal annealing, in which nitrogen impurities become highly mobile and end up pairing with the less mobile nickel ones. We considered centers with nickel in interstitial, substitutional, and divacancy sites complexing with nitrogen. According to fig. 2, the  $\text{Ni}_i\text{N}_s$  center has Ni and N atoms respectively in sites 6 and 1 and the  $\text{Ni}_s\text{N}_s$  center has Ni and N atoms respectively in sites 3 and 4. Table IV presents the results for Ni-N pairs.

Figure 8 describes the electronic structure of Ni-N complexes as resulting from an inter-

action of the energy eigenvalues of the impurities in isolated configurations. For the  $(\text{Ni}_s\text{N}_s)^0$  complex, there is a hybridization between 3d-related gap states of  $\text{Ni}_s$  with those 2p-related ones of  $\text{N}_s$ . This indicates a typical covalent interaction between those two impurities<sup>31,32</sup>. Despite this hybridization, the highest occupied energy level in the  $(\text{Ni}_s\text{N}_s)^0$  complex has an  $e$  representation, with a prevailing 3d character. On the other hand, for the  $(\text{Ni}_i\text{N}_s)^0$  complex, the electronic structure results from a weaker interaction between the states of the isolated impurities, more consistent with an ionic model<sup>24</sup>. In this last case, the highest occupied level has both 3d-related Ni and 2p-related N characters.

Table IV presents the results for complexes involving nickel and nitrogen impurities in a divacancy site. We considered two possible configurations, according to the proposed models for the NE1 and NE8 active centers described in table I. The  $\text{NVNiVN}$  complex involves the precursor  $\text{VNiV}$  plus two nitrogen atoms in diametrically opposed positions, replacing two of the nickel six nearest neighboring carbon atoms. The  $\text{N}_2\text{VNiVN}_2$  complex has four substitutional nitrogen atoms, replacing four of those nearest neighboring carbon atoms. The electronic structure of those two centers shows a strong covalent interaction between the divacancy-related orbitals and the nitrogen-related ones, which is similar to what is observed for complexes involving cobalt-nitrogen complexes in diamond<sup>33</sup>. Nitrogen incorporation into the precursor substantially alters the electronic structure of that center. This shows that the current interpretation, in which nitrogen atoms play a role of only donating electrons to the precursor, is not valid.

## V. DISCUSSIONS AND CONCLUSIONS

The results are now discussed in the context of the experimentally identified active centers observed in synthetic diamond. In a previous investigation, we have shown that the microscopic configuration of a substitutional nickel in the negative charge state  $(\text{Ni}_s^-)$  was consistent with the properties of the W8 center<sup>8,34</sup>, including symmetry, spin, and hyperfine parameters. Additionally, we have shown that the previously proposed microscopic models for the NIRIM centers, described in table I, based on interstitial nickel impurities, were not consistent. For example, the NIRIM-1 center could be better explained by an isolated substitutional nickel in the positive charge state  $(\text{Ni}_s^+)^{8,16}$ , although this investigation finds a number of other configurations which are also consistent with the NIRIM-1 symmetry and

spin.

For the NIRIM-2 center, a direct comparison between theory and experiment was more complicated. One of the proposed microscopic models for the NIRIM-2 center was an interstitial nickel with a nearby vacancy<sup>15</sup>. Theoretical investigations showed that this configuration is unstable<sup>8</sup>, such that the interstitial nickel migrates toward the vacant site, becoming a substitutional impurity. This would be fully expected considering defect energetics, since the formation energy of substitutional nickel is considerably lower than that of an interstitial one. We have previously suggested that isolated interstitial nickel in the positive charge state ( $\text{Ni}_i^+$ ) could explain some of the properties of the NIRIM-2 center<sup>8</sup>. This investigation shows that  $\text{Ni}_i^+$  is unstable in trigonal symmetry, lowering to a  $C_1$  one. However, the energy gain from this symmetry lowering is only 0.2 eV, and the final configuration is not far from a trigonal symmetry. Recently, it has been proposed that NIRIM-2 should involve interstitial nickel with a next nearest neighboring boron atom<sup>16</sup>. The results for this proposed configuration,  $(\text{Ni}_i\text{CB}_s)^0$ , are fully consistent with the experimental data for NIRIM-2 in terms of symmetry and spin. Another center, involving boron and substitutional nickel,  $(\text{Ni}_s\otimes\text{B}_s)^0$ , also provides results consistent with experimental data of NIRIM-2. This last configuration would be a strong candidate to explain the NIRIM-2 center since it involves substitutional nickel, and formation energy is considerably smaller than that for a pair involving interstitial nickel. A definite answer on the NIRIM-2 microscopic model could be achieved if future experiments could resolve the Ni-hyperfine parameters, since according to table III, those parameters are considerably different for those two configurations.

Another center has been associated to nickel-boron pairs. The NOL1 center, probably the same as the NIRIM-5 center, has been found in heavily boron-doped diamond<sup>16,19</sup>. The center has trigonal symmetry and  $S=1$ . By inspection of our results, the  $(\text{Ni}_i\text{B}_s)^+$  complex, suggested by<sup>19</sup> as the microscopic structure of this active center, is fully consistent with the experimental data. Another complex involving interstitial nickel,  $(\text{Ni}_i\otimes\text{B}_s)^+$ , is also consistent with experimental data. Complexes involving substitutional nickel could also describe the properties of the NOL1 center. The  $(\text{Ni}_s\text{B}_s)^+$  complex, suggested in Ref.<sup>16</sup>, is diamagnetic and cannot explain the NOL1 results. However, the same complex in a negative charge state,  $(\text{Ni}_s\text{B}_s)^-$ , is fully consistent with the experimental data. Although this center has been only observed in heavily boron-doped diamond, our results indicate that nickel in isolated configurations,  $\text{Ni}_s^{2-}$  or  $\text{Ni}_i^{2+}$ , are also consistent with the experimental data. In the case of

the  $\text{Ni}_i^{2+}$ , the high concentration of boron would only be required to place the Fermi level near the valence band top to access the 2+ charge state, and not necessarily participating into the complex. In order to clarify this, EPR experiments should be performed to observe the hyperfine parameters in nickel and boron nuclei.

For the NE4 centers, experiments<sup>19</sup> have suggested a microscopic structure given by a nickel impurity in a divacancy site in the negative charge state  $(\text{VNiV})^-$ . Our results for this configuration give a trigonal symmetry and a spin  $S=1/2$ , both results consistent with the experimental findings. The NE4\* center<sup>20</sup>, from table I, has been suggested to be formed by  $(\text{VNiV})^0$ . Our results corroborate that suggestion, although they indicate a trigonal symmetry, while experiments suggested a rhombohedral one. Moreover, our calculations found a hyperfine parameter ( $A_\perp$ ) of 60 MHz in the nearest neighboring carbon atoms, very close to the experimental value of 79 MHz<sup>20</sup>.

The NE1 and NE8 centers have been suggested to be formed by nickel-nitrogen complexes in a divacancy site<sup>21</sup>. Our results, in terms of spin and symmetry, for the  $(\text{NVNiVN})^-$  and  $(\text{N}_2\text{VNiVN}_2)^+$  complexes are fully consistent with the experimental data and the proposed microscopic configurations. However, according to table IV, the  $(\text{NVNiVN})^+$  and  $(\text{N}_2\text{VNiVN}_2)^-$  complexes also provide results consistent with those data. However, experiments<sup>21</sup> could not resolve the Ni-related hyperfine fields, in order to compare with the values presented in table IV. On the other hand, those experiments have identified hyperfine fields in the nitrogen and the nearest neighboring carbon nuclei. For the NE1 center, the experimental values for those fields are  $A_\parallel(\text{N}) = 59$ ,  $A_\perp(\text{N}) = 40$ ,  $A_\parallel(\text{C}) = 49$ , and  $A_\perp(\text{C}) = 31$  MHz. For the  $(\text{NVNiVN})^-$  complex, our results provide  $A_\parallel(\text{N}) = 42$  and  $A_\perp(\text{N}) = 17$  MHz and negligible values in the carbon nuclei. For the  $(\text{NVNiVN})^+$  complex, our results provide  $A_\parallel(\text{C}) = 92$  and  $A_\perp(\text{C}) = 40$  MHz and negligible values in the nitrogen nuclei. Therefore, it was not possible to make a final remark on the microscopic structure of the NE1 center. For the  $(\text{N}_2\text{VNiVN}_2)^+$  complex, hyperfine fields in the nitrogen and carbon nuclei are fully consistent with experimental values of the NE8 center. Finally, the  $(\text{Ni}_s\text{N}_s)^-$  complex has been proposed as the microscopic structure of the AB5 center<sup>22</sup>. From all the complexes involving nickel and nitrogen considered here, that configuration was the only one consistent with the experimental results of the AB5 center.

In summary, we have performed a theoretical investigation on nickel-related complexes in diamond, in terms of electronic structure and hyperfine fields. We have explored several

microscopic configurations that could explain the experimental data on EPR active centers in synthetic diamond, confirming or discarding some of the previously proposed microscopic models and suggesting new ones. These results provide a comprehensive picture on Ni-related active centers in diamond using a single theoretical methodology.

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### APPENDIX: CALCULATION OF THE HYPERFINE TENSORS

The EPR data can provide important information related to electrically active centers in semiconductors, such as symmetry, spin, gyromagnetic factor, and in some stances the atomic composition of those centers. The hyperfine spectrum of a center results from an interaction between nuclear magnetic moments ( $\vec{\mu}_I$ ) and the moments of unpaired electrons. The crystalline field, in which the impurity (or other defects) is immersed, is generally enough strong to quench the respective orbital moment. However, it has been shown that in the case of transition metal impurities, the orbital moment is not fully quenched by the crystal field, generating, in some cases, a large energy anisotropy. Most of the theoretical investigations have neglected this anisotropic contribution, but it is very important for systems such as those investigated here.

The hyperfine fields were computed using the implementation from the WIEN2k package<sup>26</sup> that uses a scalar-relativistic approximation<sup>35</sup>. According to that approach, the hyperfine magnetic field ( $\vec{B}_{\text{hf}}$ ) is computed considering three components: the Fermi contact ( $\vec{B}_{\text{c}}$ ), the dipolar ( $\vec{B}_{\text{dip}}$ ), and the orbital ( $\vec{B}_{\text{orb}}$ ) terms.

$$\vec{B}_{\text{hf}} = \vec{B}_{\text{c}} + \vec{B}_{\text{dip}} + \vec{B}_{\text{orb}}, \quad (1)$$

These three components are given in terms of the the angular ( $\vec{L}$ ) and spin ( $\vec{S}$ ) electronic

moments (in  $\hbar$  unities) and the Bohr magneton ( $\beta_e = e\hbar/2m$ ):

$$\vec{B}_c = \frac{8\pi}{3}\beta_e\vec{m}_{av}, \quad (2)$$

$$\vec{B}_{\text{dip}} = -g_e\beta_e \langle \Phi \left| \frac{S(r)}{r^3} \left[ \vec{S} - 3 \left( \vec{S} \cdot \vec{r} \right) \frac{\vec{r}}{r^2} \right] \right| \Phi \rangle, \quad (3)$$

$$\vec{B}_{\text{orb}} = 2\beta_e \langle \Phi \left| \frac{S(r)}{r^3} \vec{L} \right| \Phi \rangle, \quad (4)$$

where  $\Phi$  is the relativistic large component of the wavefunction and  $S(r)$  is the reciprocal relativistic mass enhancement:

$$S(r) = \left[ 1 + \frac{\varepsilon - V(r)}{2mc^2} \right]^{-1}, \quad (5)$$

where  $\varepsilon$  and  $V(r)$  are respectively the kinetic energy and the Coulomb potential.

$\vec{m}_{av}$  is the average nuclear magnetization,

$$\begin{aligned} \vec{m}_{av} &= \int \delta_T(\vec{r}') \vec{m}(\vec{r}') d\vec{r}' = \\ &= \int \delta_T(\vec{r}') \langle \Phi | \vec{\sigma} \delta(\vec{r} - \vec{r}') | \Phi \rangle d\vec{r}' \end{aligned} \quad (6)$$

where  $\delta_T(\vec{r}')$  is given in terms of the Thomas radius ( $r_T = Ze^2/mc^2$ ):

$$\delta_T(\vec{r}') = \frac{1}{4\pi r^2} \frac{r_T}{[2r(1 + \varepsilon/2mc^2) + r_T]} \quad (7)$$

and  $\vec{\sigma}$  are the Pauli matrices.

The splitting in energy resulting from the interaction between the hyperfine magnetic fields ( $\vec{B}_{\text{hf}}$ ) and  $\vec{\mu}_I$  is described by:

$$E = -\vec{\mu}_I \cdot \vec{B}_{\text{hf}}. \quad (8)$$

This splitting in energy may be described in terms of a spin Hamiltonian ( $H$ ). The eigenvalues of this Hamiltonian provide information on the separation between absorption lines in the magnetic spectra.

$$H = \vec{J} \cdot \overleftrightarrow{A} \cdot \vec{I} = (\vec{L} + \vec{S}) \cdot \overleftrightarrow{A} \cdot \vec{I} \quad (9)$$

where  $\vec{I}$  is the nuclear spin and  $\overleftrightarrow{A}$  is a  $(3 \times 3)$  hyperfine interaction tensor.

The hyperfine interaction tensor has the following components  $A_{ij}$ :

$$\begin{aligned} A_{ij} &= a_{ij}^c \delta_{ij} + a_{ij}^{\text{dip}} + a_{ij}^{\text{orb}}, \quad \text{with} \\ \sum_i a_{ii}^{\text{dip}} &= 0 \quad \text{and} \quad \sum_i a_{ii}^{\text{orb}} \neq 0. \end{aligned} \quad (10)$$

In an experiment, when the direction of the external static magnetic field ( $\hat{n} = \sin \theta \cos \varphi \hat{i} + \sin \theta \sin \varphi \hat{j} + \cos \theta \hat{k}$ ) is varied with respect to the sample axis, the relevant quantity is the projection of the hyperfine interaction tensor in that direction:

$$\begin{aligned}
A(\theta, \varphi) &= \hat{n} \cdot \overleftrightarrow{\mathbf{A}} \cdot \hat{n} = \\
&= A_{11} \sin^2 \theta \cos^2 \varphi + (A_{12} + A_{21}) \sin \theta \cos \varphi \sin \varphi + \\
&+ A_{22} \sin^2 \theta \sin^2 \varphi + (A_{23} + A_{32}) \cos \theta \sin \theta \sin \varphi + \\
&+ A_{33} \cos^2 \theta + (A_{13} + A_{31}) \cos \theta \sin \theta \cos \varphi.
\end{aligned} \tag{11}$$

By choosing a convenient set of six directions, *i.e.* six sets of  $(\theta, \varphi)$ , the values of  $A(\theta, \varphi)$  in those directions allow to build the hyperfine interaction tensor. It can be later diagonalized to obtain the three principal values, also called hyperfine parameters ( $A_1$ ,  $A_2$ , and  $A_3$ ), and their respective eigenvectors.

The hyperfine tensor  $\overleftrightarrow{\mathbf{A}}$  is given in terms of:

$$\overleftrightarrow{\mathbf{A}} = a^c \mathbb{1} + \overleftrightarrow{\mathbf{B}} + \overleftrightarrow{\mathbf{C}}, \tag{12}$$

where  $\mathbb{1}$  is the unitary tensor, and  $a^c$  is the contact term,  $\overleftrightarrow{\mathbf{B}}$  is a traceless anisotropic tensor related to the dipolar interaction, and  $\overleftrightarrow{\mathbf{C}}$  is an anisotropic tensor related to the orbital interaction.

If the angular magnetic moment is quenched, the isotropic part of the hyperfine tensor is exactly the Fermi contact interaction and the anisotropic part is the dipolar interaction. However, if the angular moment is not quenched, there should be a contribution from this interaction to the hyperfine tensor changing both the dipolar and contact terms. In this investigation, we observed that the hyperfine orbital field is generally relevant and cannot be neglected. This was result of the spin-orbit coupling in the 3d localized orbitals, which are deformed due to the crystalline field.

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TABLE I: Experimental data on the electrically active centers of Ni-related defects in diamond. The table presents the symmetry, spin, and proposed microscopic model. X represents an unknown specie (a vacancy or impurity), and V represents a vacancy. A list of additional relevant active centers in diamond can be found in Reference<sup>23</sup>.

Label	Sym.	S	Model
W8	tetrahedral	3/2	$\text{Ni}_s^-$ <sup>(a)</sup>
NIRIM-1	trigonal ( $T < 25\text{K}$ )	1/2	$\text{Ni}_i^+$ <sup>(b)</sup> , $\text{Ni}_s^+$ <sup>(c),(d)</sup>
NIRIM-2	trigonal	1/2	$\text{Ni}_i^+ \text{-X}$ <sup>(b)</sup> , $\text{Ni}_i^+ \text{CB}_s^-$ <sup>(d)</sup>
NE4	trigonal	1/2	$(\text{VNiV})^-$ <sup>(e)</sup>
NE4*	rhombohedral	1	$(\text{VNiV})^0$ <sup>(f)</sup>
NE1	monoclinic	1/2	$(\text{NVNiVN})^-$ <sup>(g)</sup>
NE8	monoclinic	1/2	$(\text{N}_2\text{VNiVN}_2)^+$ <sup>(g)</sup>
NOL1	trigonal	1	$\text{Ni}_s^+ \text{B}_s^0$ <sup>(c)</sup> , $\text{Ni}_i^{2+} \text{B}_s^-$ <sup>(g)</sup>
AB5	trigonal	1	$\text{Ni}_s^{2-} \text{-N}_s^+$ <sup>(h)</sup>

<sup>(a)</sup> Reference<sup>13</sup>, <sup>(b)</sup> Reference<sup>15</sup>, <sup>(c)</sup> Reference<sup>8</sup>, <sup>(d)</sup> Reference<sup>16</sup>,  
<sup>(e)</sup> Reference<sup>19</sup>, <sup>(f)</sup> Reference<sup>20</sup>, <sup>(g)</sup> Reference<sup>21</sup>, <sup>(h)</sup> Reference<sup>22</sup>.

TABLE II: Results for isolated Ni and Ni-divacancy complexes in diamond: symmetry, spin (S), multiplet ground state ( $^{2S+1}\Gamma$ ), formation energies ( $E_F$ ), and transition energies ( $E_t$  with relation to the valence band top  $\varepsilon_v$ ). Here  $\epsilon_F$  is the Fermi energy. The table also presents the calculated hyperfine parameters ( $A_i$ ,  $i = 1, 2, 3$ ) in the  $^{61}\text{Ni}$  nucleus. Energies and hyperfine parameters are given in eV and MHz, respectively.

Center	Sym.	S	$^{2S+1}\Gamma$	$E_F$	$E_t$	$A_1$	$A_2$	$A_3$
$\text{Ni}_s^{2+}$	$T_d$	0	$^1A_1$	$3.9 + 2\epsilon_F$	$2.0 (2 + /+)$	—	—	—
$\text{Ni}_s^+$	$C_{3v}$	1/2	$^2A_1$	$5.9 + \epsilon_F$	$2.6 (+/0)$	123	-36	-36
$\text{Ni}_s^{0*}$	$C_{3v}$	1	$^3E$	8.6		52	9	9
$\text{Ni}_s^0$	$C_1$	1	$^3A$	8.5		45	18	4
$\text{Ni}_s^-$	$T_d$	3/2	$^4A_2$	$11.5 - \epsilon_F$	$3.0 (0/-)$	18	18	18
$\text{Ni}_s^{2-}$	$C_{3v}$	1	$^3A$	$15.5 - 2\epsilon_F$	$4.0 (-/2-)$	-99	21	21
$\text{Ni}_i^{2+}$	$C_{3v}$	1	$^3A$	$15.5 + 2\epsilon_F$	$0.6 (2 + /+)$	32	2	2
$\text{Ni}_i^{+*}$	$C_{3v}$	1/2	$^2E$	$16.3 + \epsilon_F$		29	15	15
$\text{Ni}_i^+$	$C_{1h}$	1/2	$^2A$	$16.1 + \epsilon_F$	$1.1 (+/0)$	66	19	17
$\text{Ni}_i^0$	$T_d$	0	$^1A_1$	17.2		—	—	—
$(\text{VNiV})^+$	$C_{2h}$	1/2	$^2A$	$5.2 + \epsilon_F$	$0.2 (+/0)$	51	17	14
$(\text{VNiV})^0$	$D_{3d}$	1	$^3A_{2u}$	5.4		6	33	33
$(\text{VNiV})^-$	$C_{2h}$	1/2	$^2A$	$6.2 - \epsilon_F$	$0.8 (0/-)$	18	-52	-22
$(\text{VNiV})^{2-}$	$D_{3d}$	0	$^1A$	$7.3 - 2\epsilon_F$	$1.1 (-/2-)$	—	—	—

TABLE III: Results for nickel-boron complexes in diamond: symmetry, spin (S), multiplet ground state ( $^{2S+1}\Gamma$ ), formation ( $E_F$ ) and transition energies ( $E_t$  with relation to  $\varepsilon_v$ ). The table also presents the calculated hyperfine parameters ( $A_i$ ) in the  $^{61}\text{Ni}$  nucleus.

Center	Sym.	S	$^{2S+1}\Gamma$	$E_F$	$E_t$	$A_1$	$A_2$	$A_3$
$(\text{Ni}_i\text{B}_s)^+$	$C_{3v}$	1	$^3A$	$14.8 + \epsilon_F$	1.1 (+/0)	7	35	35
$(\text{Ni}_i\text{B}_s)^{0*}$	$C_{3v}$	1/2	$^2E$	16.1		76	-62	-62
$(\text{Ni}_i\text{B}_s)^0$	$C_1$	1/2	$^2A$	15.9		40	-56	-27
$(\text{Ni}_i\text{B}_s)^-$	$C_{3v}$	0	$^1A_1$	$17.3 - \epsilon_F$	1.4 (0/-)	-	-	-
$(\text{Ni}_i\text{CB}_s)^+$	$C_{3v}$	0	$^1A_1$	$15.4 + \epsilon_F$	1.8 (+/0)	-	-	-
$(\text{Ni}_i\text{CB}_s)^0$	$C_{3v}$	1/2	$^2A_1$	17.2		21	-14	-14
$(\text{Ni}_i\text{CB}_s)^-$	$C_{3v}$	0	$^1A_1$	$18.2 - \epsilon_F$	1.4 (+/-)	-	-	-
$(\text{Ni}_i \otimes \text{B}_s)^+$	$C_{3v}$	1	$^3A$	$15.9 + \epsilon_F$	0.5 (+/0)	7	-17	-17
$(\text{Ni}_i \otimes \text{B}_s)^0$	$C_1$	1/2	$^2A$	16.4		-5	50	46
$(\text{Ni}_i \otimes \text{B}_s)^-$	$C_{3v}$	0	$^1A_1$	$17.9 - \epsilon_F$	1.5 (0/-)	-	-	-
$(\text{Ni}_s\text{B}_s)^+$	$C_{3v}$	0	$^1A_1$	$3.5 + \epsilon_F$	2.6 (+/0)	-	-	-
$(\text{Ni}_s\text{B}_s)^0$	$C_1$	1/2	$^2A$	6.1		-99	55	-32
$(\text{Ni}_s\text{B}_s)^-$	$C_{3v}$	1	$^3A_1$	$9.0 - \epsilon_F$	2.9 (0/-)	85	1	1
$(\text{Ni}_s \otimes \text{B}_s)^+$	$C_{3v}$	0	$^1A_1$	$4.7 + \epsilon_F$	2.1 (+/0)	-	-	-
$(\text{Ni}_s \otimes \text{B}_s)^0$	$C_{3v}$	1/2	$^2A_1$	6.8		-120	48	48
$(\text{Ni}_s \otimes \text{B}_s)^-$	$C_1$	1	$^3A$	$9.2 - \epsilon_F$	2.4 (0/-)	42	18	8

TABLE IV: Results for nickel-nitrogen complexes in diamond: symmetry, spin (S), multiplet ground state ( $^{2S+1}\Gamma$ ), formation ( $E_F$ ) and transition energies ( $E_t$  with relation to  $\varepsilon_v$ ). The table also presents the calculated hyperfine parameters ( $A_i$ ) in the  $^{61}\text{Ni}$  nucleus.

Center	Sym.	S	$^{2S+1}\Gamma$	$E_F$	$E_t$	$A_1$	$A_2$	$A_3$
$(\text{Ni}_i\text{N}_s)^+$	$C_{3v}$	0	$^1A_1$	$15.8 + \epsilon_F$	$3.2 (+/0)$	—	—	—
$(\text{Ni}_i\text{N}_s)^0$	$C_{3v}$	1/2	$^2A_1$	19.0		82	14	14
$(\text{Ni}_i\text{N}_s)^-$	$C_{3v}$	0	$^1A_1$	$22.5 - \epsilon_F$	$3.5 (0/-)$	—	—	—
$(\text{Ni}_s\text{N}_s)^+$	$C_{3v}$	0	$^1A_1$	$6.0 + \epsilon_F$	$3.1 (+/0)$	—	—	—
$(\text{Ni}_s\text{N}_s)^0$	$C_1$	1/2	$^2A$	9.1		-110	70	-30
$(\text{Ni}_s\text{N}_s)^-$	$C_{3v}$	1	$^3A_1$	$12.6 - \epsilon_F$	$3.5 (0/-)$	-58	2	2
$(\text{N } V\text{Ni } V\text{N})^+$	$C_{2h}$	1/2	$^2A$	$3.2 + \epsilon_F$	$1.3 (+/0)$	28	-20	-24
$(\text{N } V\text{Ni } V\text{N})^0$	$C_{2h}$	0	$^1A$	4.5		—	—	—
$(\text{N } V\text{Ni } V\text{N})^-$	$C_{2h}$	1/2	$^2A$	$7.5 - \epsilon_F$	$3.0 (0/-)$	177	58	43
$(\text{N}_2 V\text{Ni } V\text{N}_2)^+$	$C_{2h}$	1/2	$^2A$	$2.7 + \epsilon_F$	$3.7 (+/0)$	-167	-18	-15
$(\text{N}_2 V\text{Ni } V\text{N}_2)^0$	$C_{2h}$	0	$^1A$	6.4		—	—	—
$(\text{N}_2 V\text{Ni } V\text{N}_2)^-$	$C_{2h}$	1/2	$^2A$	$10.7 - \epsilon_F$	$4.3 (0/-)$	1	-5	-4

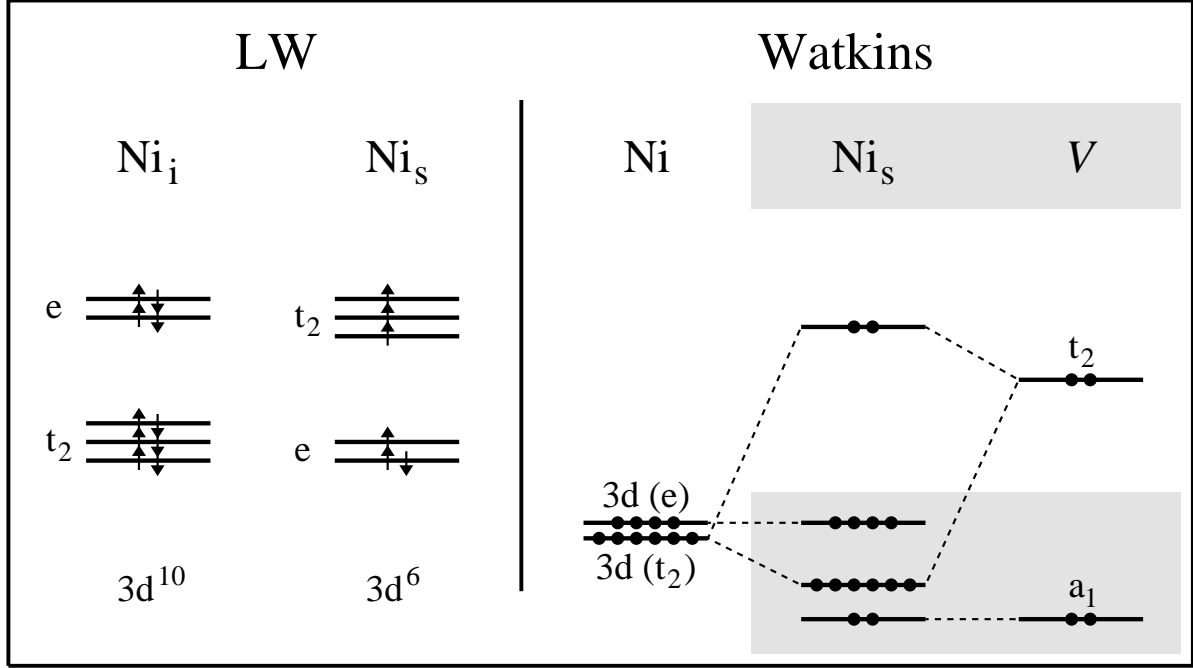


FIG. 1: Schematic representation of the gap states for an isolated interstitial (Ni<sub>i</sub>) or substitutional (Ni<sub>s</sub>) nickel in neutral charge state, according to LW<sup>11</sup> and Watkins (vacancy)<sup>12</sup> models. The ↑ and ↓ arrows represent the spin up and down, respectively. Gray regions represent the valence and conduction host bands. For simplicity, the system is considered in a tetrahedral symmetry, neglecting distortions.

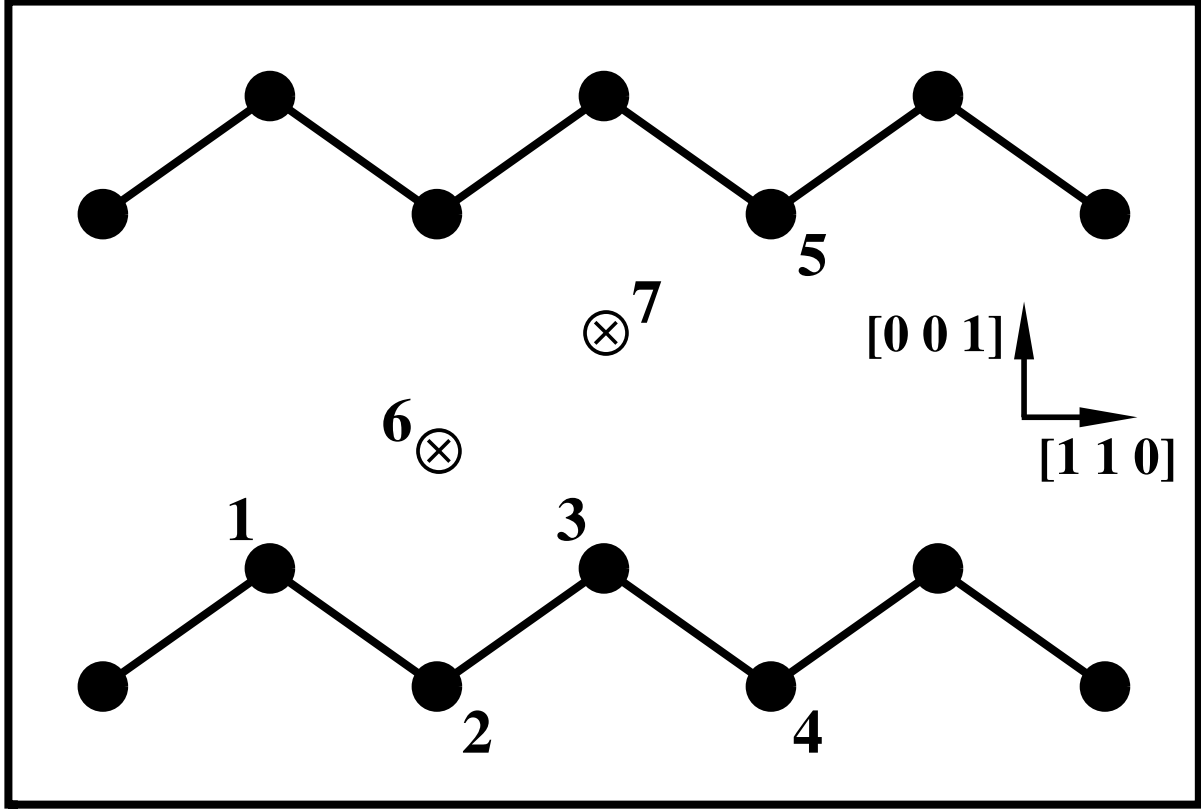


FIG. 2: Representation of the diamond lattice in the  $(1\bar{1}0)$  plane. Carbon atoms are represented by black circles. Labels, from 1 to 5, indicate the crystal site positions where the impurities could be placed. The figure also shows two tetrahedral interstitial sites (6 and 7), represented by the  $\otimes$  symbol, in the  $[111]$  direction.

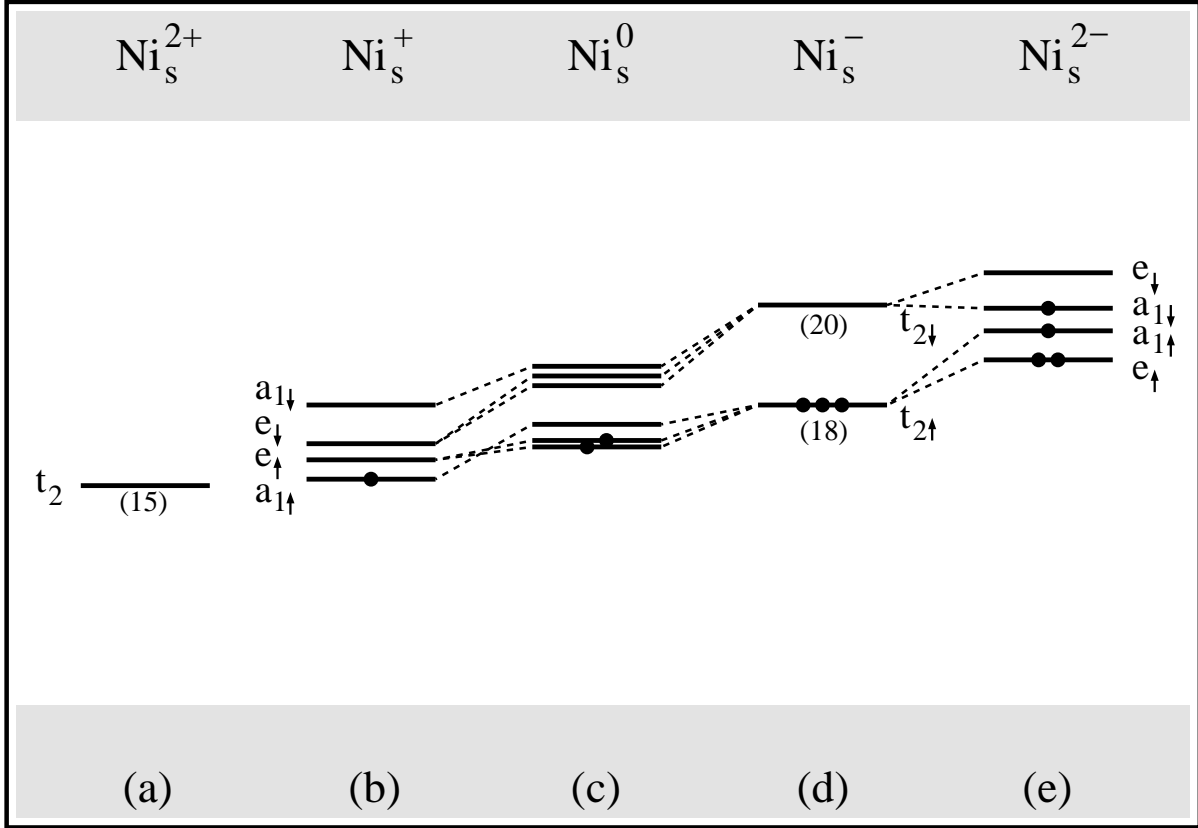


FIG. 3: The Kohn-Sham spin-polarized energy eigenvalues (around the  $\Gamma$  point) representing the  $3d$ -related Ni levels in the gap region for isolated substitutional nickel in different charge states: (a)  $\text{Ni}_s^{2+}$ , (b)  $\text{Ni}_s^+$ , (c)  $\text{Ni}_s^0$ , (d)  $\text{Ni}_s^-$ , and (e)  $\text{Ni}_s^{2-}$ . Levels with spin up and down are represented by  $\uparrow$  and  $\downarrow$  arrows, respectively. The occupation of the gap levels is given by the number of filled circles. Numbers in parenthesis represent the  $d$ -character percentage of charge inside the Ni atomic sphere.



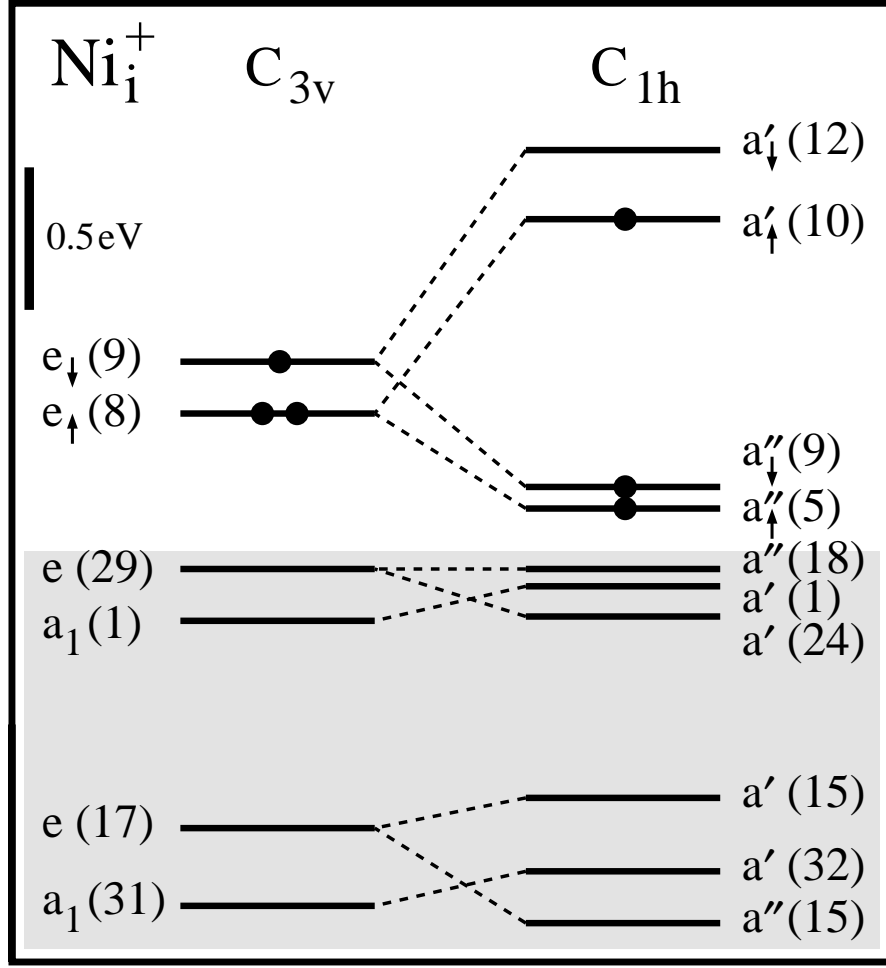


FIG. 4: The energy eigenvalues representing the  $3d$ -related Ni levels for isolated interstitial nickel in the positive charge state in  $C_{3v}$  and  $C_{1h}$  symmetries. Levels with spin up and down are represented by  $\uparrow$  and  $\downarrow$  arrows, respectively. The occupation of the gap levels is given by the number of filled circles. The numbers in parenthesis represent the  $d$ -character percentage of charge inside the Ni atomic sphere.

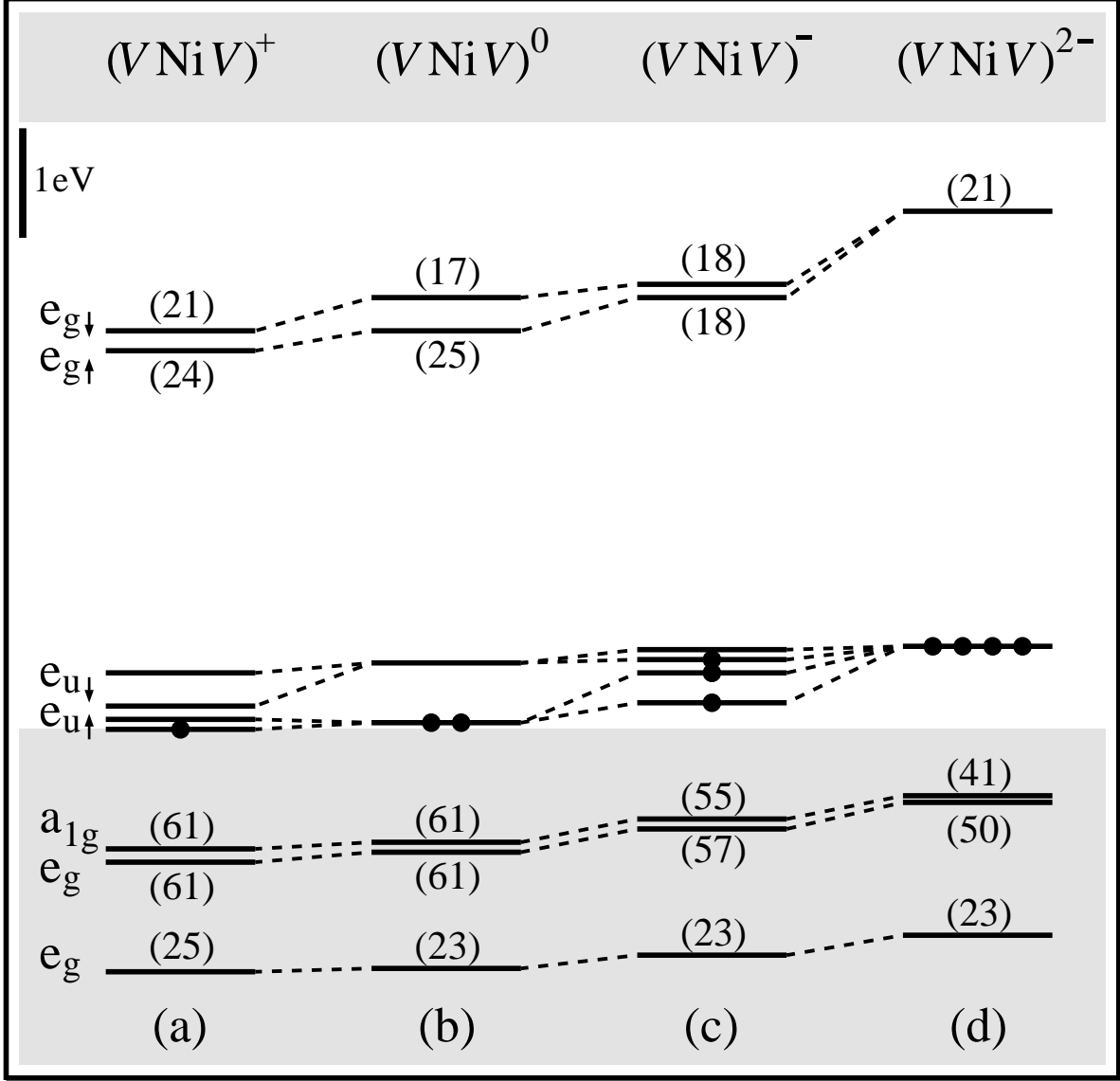


FIG. 5: The energy eigenvalues representing the 3d-related Ni levels in the gap region for the Ni-divacancy complexes: (a)  $(VNiV)^+$ , (b)  $(VNiV)^0$ , (c)  $(VNiV)^-$ , and (d)  $(VNiV)^{2-}$  centers. The occupation of the gap levels is given by the number of filled circles. The numbers in parenthesis represent the  $d$ -character percentage of charge inside the nickel atomic sphere. Levels with spin up and down are represented by  $\uparrow$  and  $\downarrow$  arrows, respectively.

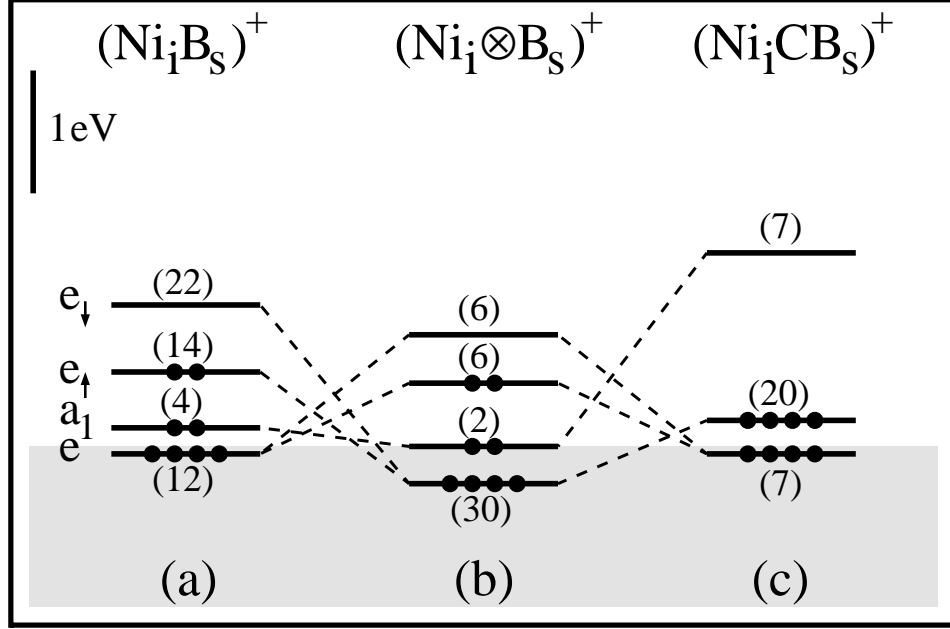


FIG. 6: The energy eigenvalues in the gap region for three configurations involving interstitial nickel-substitutional boron complexes in the positive charge state: (a)  $(\text{Ni}_i \text{B}_s)^+$ , (b)  $(\text{Ni}_i \otimes \text{B}_s)^+$ , and (c)  $(\text{Ni}_i \text{CB}_s)^+$ . The occupation of the levels is given by the number of filled circles. The numbers in parenthesis represent the  $d$ -character percentage of charge inside the nickel atomic sphere.

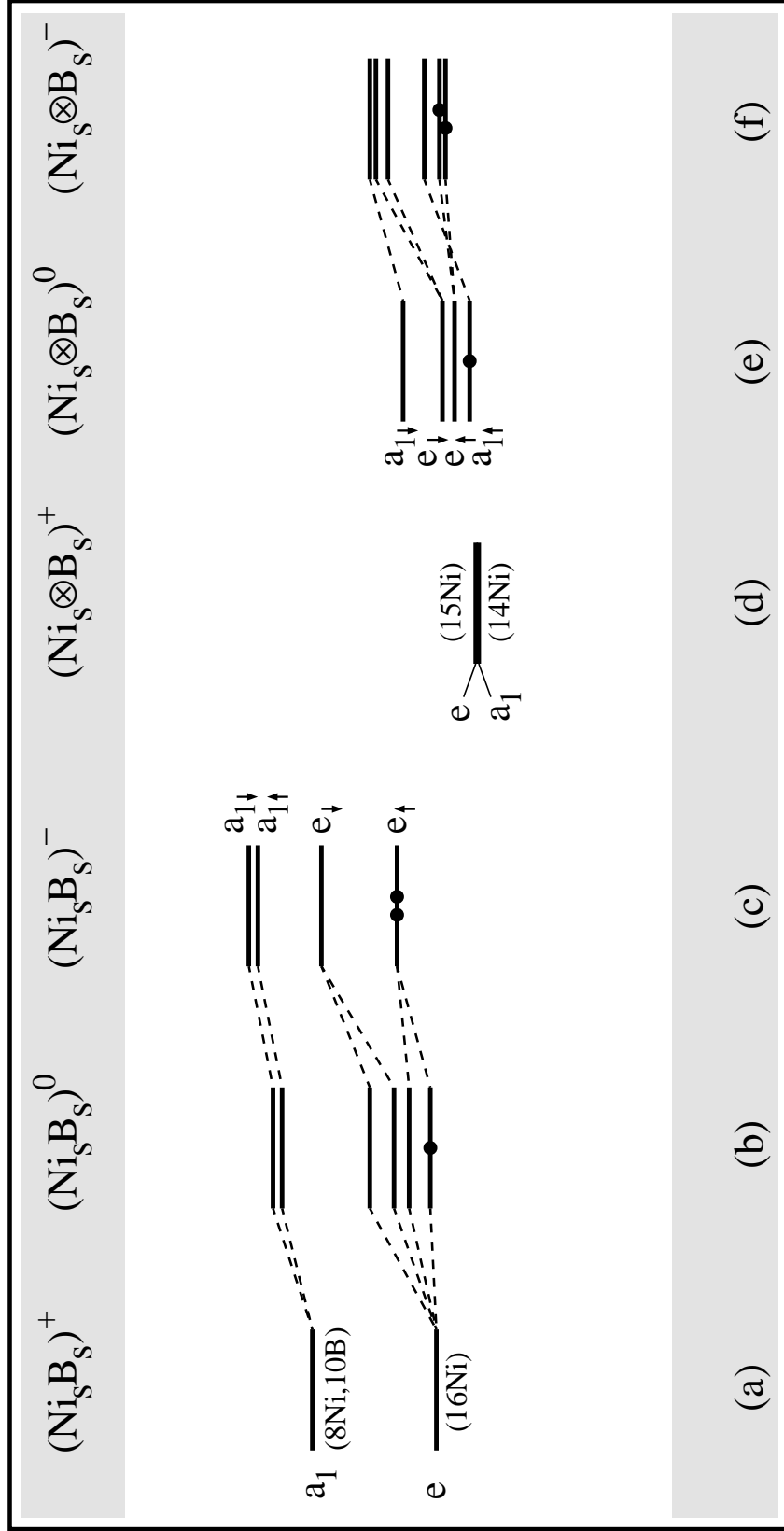


FIG. 7: The energy eigenvalues for the substitutional nickel-substitutional boron complexes in two configurations: (a,b,c) for the  $\text{Ni}_s \text{B}_s$  complex and (d,e,f) for the  $\text{Ni}_s \otimes \text{B}_s$  complex. The occupation of the gap levels is given by the number of filled circles. The numbers in parenthesis represent the  $d$ -character ( $p$ -character) percentage of charge inside the nickel (boron) atomic sphere. Levels with

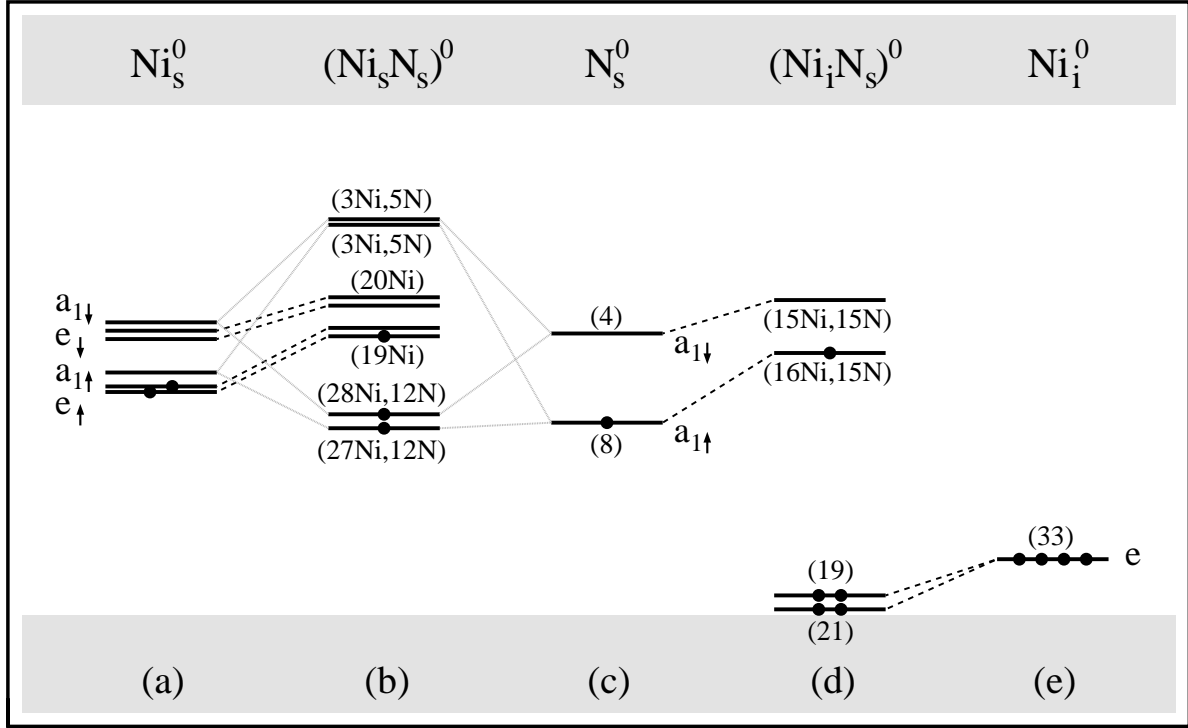


FIG. 8: The energy eigenvalues for the  $(\text{Ni}_i \text{N}_s)$  and  $(\text{Ni}_s \text{N}_s)$  complexes in the neutral charge state. The figure shows that the electronic structure of those centers results from hybridization between the  $2p$  nitrogen with  $3d$  nickel levels coming from its precursors in isolated configurations.